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The Molecular Structure of Cyclopropene, C_3H_4

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(Received May 9, 1952)

Cyclopropene, C_3H_4 , has been investigated by the electron diffraction method. The cyclic structure is confirmed and the following interatomic distances and angles are found: C—C, 1.52 ± 0.02 Å; C=C, 1.28 ± 0.04 Å; <C—H>, 1.08 ± 0.04 Å; \angle H—C—H, 118° (assumed); \angle C=C—H, $152 \pm 12^\circ$.

SOME years ago, Dr. E. R. Buchman and Dr. M. J. Schlatter suggested that the structure of the unusual hydrocarbon cyclopropene,¹ C_3H_4 , might be

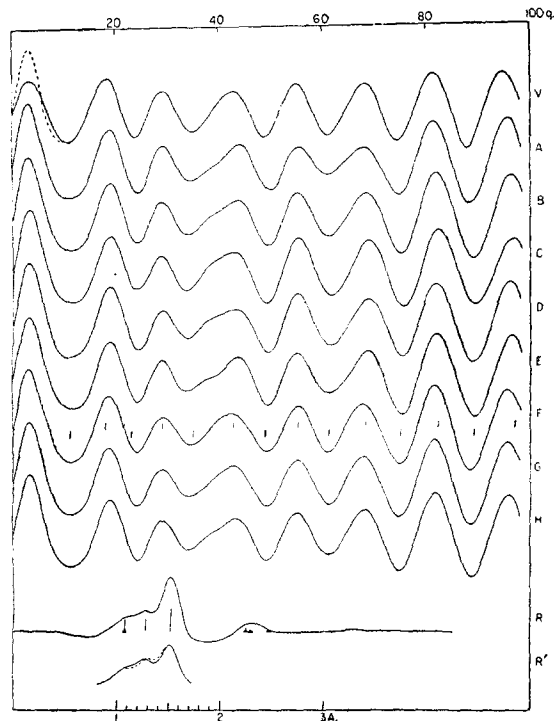


FIG. 1. Electron diffraction curves for cyclopropene, C_3H_4 . V. Visual curve. (The full curve was used for calculation of R. The broken curve shows the first feature as given by the theoretical curves.) A—H. Theoretical curves.

Model	C—C	C=C	<C—H>	<C···H>	\angle HCH $^\circ$	\angle C=C—H $^\circ$
A	1.52	1.31	1.08	2.29		
B	1.52	1.28	1.08	2.29		
C	1.52	1.25	1.08	2.29		
D	1.52	1.28	1.11	2.29		
E	1.52	1.28	1.08	2.32		
F	1.53	1.29	1.09		118	147.5
G	1.53	1.29	1.09		118	157.5
H	1.53	1.29	1.09		118	167.5

R. Radial distribution curve from V. R'. Synthesis of portion of R as sum of Gaussian curves. C—C, 1.52 Å, <C—H>, 1.08 Å, C=C, 1.28 Å (full line). C—C, 1.52 Å, <C—H>, 1.08 Å, C=C, 1.30 Å (broken line).

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† Contribution No. 1690.

¹ For method of preparation and earlier references see M. J. Schlatter, J. Am. Chem. Soc. 63, 1733 (1941).

confirmed by electron diffraction investigation. We wish to report here on the interpretation of a set of electron diffraction photographs, prepared in 1940, of a sample of cyclopropene provided by them (see Table I):

The structure is confirmed by the radial distribution curve² of Fig. 1, particularly by the absence of any strong peak past 2.5 Å. The peak extending from 0.9 to 1.7 Å is, moreover, evidently composed of C—C, C=C, and C—H interactions in about the correct proportions. The C—C distance is obviously close to 1.53 Å, but the other two interactions are not resolved. On the assumption of C—C = 1.52 Å and C—H = 1.08 Å, analysis of the composite peak in terms of three Gaussian curves of appropriate heights and widths leads to C=C = 1.29 Å.

For the correlation treatment the molecule was assumed to have symmetry C_{2v} , with all bonded C—H distances equal. For the initial models, further, the three nonbonded C···H distances were represented by a single suitably temperature-factored term. Systematic variation of the remaining shape parameters (\langle C—H>/C—C, C=C/C—C, and \langle C···H>/C—C) showed curve B to be the best of this type. Splitting the

TABLE I. Observed and calculated q values.

Model			F	G
Max	Min	q_0	q/q_0	q/q_0
1	1	10.95	(1.050)	(1.050)
		17.9	(1.039)	(1.045)
2	2	22.8	(1.053)	(1.053)
		28.95	1.002	0.998
3	3	34.8	0.991	0.980
		42.6	0.986	1.000
4	4	48.7	1.010	1.006
		55.2	1.002	0.996
5	5	61.0	1.000	1.002
		68.2	0.990	0.991
6	6	74.8	0.999	0.997
		82.15	(0.992)	(0.992)
7	7	88.95	(0.994)	(0.995)
		96.95	(0.985)	(0.985)
Mean, 8 features			0.9975	0.9962
Mean deviation			0.006	0.006
C—C, 1.52 × 0.9968 = 1.525				
C=C, 1.29 × 0.9968 = 1.286				
C—H, 1.09 × 0.9968 = 1.087				

² For experimental procedures and methods of calculation see J. D. Dunitz and V. Schomaker, J. Chem. Phys. 20, 1703 (1952).

nonbonded $C\cdots H$ distances then led to completely satisfactory agreement (curves *F* and *G*). Our final parameter values and limits of error are: $C-C$, $1.52_6 \pm 0.02$ Å; $C=C$, $1.28_6 \pm 0.04$ Å; $(\angle C-C-C, 49.9^\circ)$; $(C-H)$, $1.08_7 \pm 0.04$ Å; $\angle H-C-H$, 118° (assumed: $\angle C-C-H = \angle H-C-H$); and $\angle C=C-H$, $152 \pm 12^\circ$.

The single bonds appear to be shortened, as in other

three-membered rings,^{3,4,5} and it is interesting that the double bond is even more shortened.

³ H. G. Pfeiffer, Ph.D. thesis, California Institute of Technology, 1948.

⁴ Cunningham, Boyd, Gwinn, and LeVan, *J. Chem. Phys.* **17**, 211 (1949).

⁵ Donohue, Humphrey, and Schomaker, *J. Am. Chem. Soc.* **67**, 332 (1945).

The Asymmetric Rotor. X. The Hydrogen Sulfide Spectrum in the 5150 cm^{-1} Region*

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(Received June 3, 1952)

The absorption spectrum of hydrogen sulfide in the region from 5000 to 5250 cm^{-1} has been measured and the rotational fine structure analyzed. The structure can be accounted for as arising from two vibrational transitions yielding a type *A* band centered at 5147 cm^{-1} and a type *B* band centered at 5145 cm^{-1} . The excited state constants giving the best fit are type *A* band, $A^* = 10.04$, $B^* = 8.68$, $C^* = 4.61\text{ cm}^{-1}$; type *B* band, $A^* = 10.08$, $B^* = 8.68$, $C^* = 4.59\text{ cm}^{-1}$.

The frequencies and rotational band types indicate that these bands are the $(n_\sigma, n_\pi, n_\delta) = (110)$ (type *A*) and the lower component of the resonating pair (020) (200) (type *B*).

INTRODUCTION

THE infrared band system of hydrogen sulfide has recently been fitted to a self-consistent scheme,¹ a clue to the nature of which was the recognition of the absorption in the 5150 cm^{-1} region as too complex to be assigned to a single vibrational transition. The analysis of the rotational fine structure of this region was

undertaken to provide precise values of the frequencies of the two vibrational transitions assumed to be present and to obtain the inertial parameters of the excited states.

The experimental data presented in Fig. 1 and Table I were obtained under the same conditions used for recording the absorption in the 6290 cm^{-1} region.² The

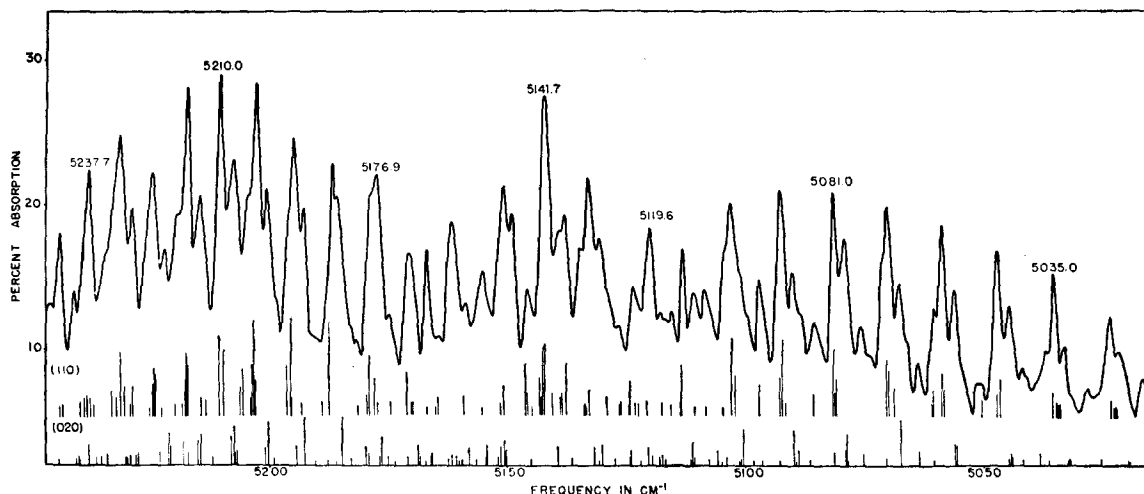


FIG. 1. Calculated and observed spectrum in the 5146 cm^{-1} region.

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† Now at the Chemistry Department, Harvard University.

¹ Allen, Cross, and King, *J. Chem. Phys.* **18**, 1412 (1950).

² Allen, Cross, and Wilson, *J. Chem. Phys.* **18**, 691 (1950).